EFFECTS ON ICE NANOCRYSTALS OF EXPOSURE TO DIFFERENT ADSORBATES

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TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1

Introduction

The Earth's early atmosphere was created by the volcanic expulsion of gases from the interior. Due to the presence of sunlight and the evolution of the life, these original compounds have been transformed. The present atmosphere is composed of a variety of substances. Nitrogen (78%) and oxygen (21%) form Ninety-nine percent of air. Their ratio has not changed for millions of years. But, the other components, such as water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and inert gases make up less than 1% of the volume of the air. The atmosphere is divided into several layers. The lowest region is the troposphere, where most human activities occur. Most atmospheric ozone is concentrated in the stratosphere, where an O_3 layer absorbs a portion of the ultraviolet radiation from the sun. Ultraviolet radiation has been linked to many harmful effects, including various types of skin cancer, cataracts, and harm to some crops, certain materials, and some forms of marine life. However, O_3 concentrations vary naturally with sunspots, the seasons, and latitude. Atmospheric scientists have recently noticed a dramatic decrease in ozone levels in the stratosphere. In January of 1993, researchers discovered that ozone levels above the northern mid latitudes were 13 to 14 percent below normal[1] (Zurer, Pamela 1993). The National Aeronautics and Space Administration (NASA) documented that in 1993 the levels of ozone were the lowest in fourteen years[1] (Zurer 1993). Many people blamed the eruption of Mount Pinatubo in the Philippines for the decrease, yet atmospheric scientists claim that chlorofluocarbons (CFCs) are the real culprits. Chlorofluocarbons are used in industry as refrigerants and are sold to the public in products such as aerosol cans. CFCs could absorb high-energy photons from sunlight and release free chlorine (Cl); once released, the chlorine could destroy stratospheric ozone through a series of reactions. However this gas phase process is too slow to explain the net atmospheric loss of O_3. This work investigated processes related to the role of heterogeneous reactions in the destruction of ozone

in the stratosphere. Specifically, the reaction of hydrogen bromide (HBr), ammonia and solid water (ice) have been investigated.

Normally ozone is continually created and destroyed via the following reactions:

$O_2 + hv \rightarrow O + O$

Where, hv is the energy of the photon of frequency v. Some of these single atoms of oxygen then combine with oxygen molecules to form a molecule of ozone (O_3).

$O + O_2 \rightarrow O_3$

Since the three atoms of oxygen in ozone are weakly bound relative to molecular oxygen, weaker ultraviolet radiation has enough energy to photodissociate ozone, but not molecular oxygen.

$O_3 + hv \rightarrow O_2 + O$

These reactions take place about 40 kilometers above the earth in the stratosphere.

It is theorized that the CFCs rise into the upper atmosphere where they are photolyzed to produce another CFC and a chlorine free radical[1] (Zurer 1993). One such reaction is:

CCl_2F_2 (CFC-12) + $hv \rightarrow CClF_2 + Cl$

Free chlorine radicals' act as catalysts, which deplete O_3 molecules in the following manner:

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

$O_3 + O \rightarrow 2O_2$ (net)

As the chlorine radical is regenerated in this process, it will destroy many other O_3 molecules by the same way.

Now, atmospheric scientists are particularly interested in ozone depletion over the frozen Antarctic continent. Satellite images show that each September a hole forms in the ozone layer over Antarctica. It lasts for a few months and starts filling up again thereafter. During the Antarctic winter, a special wind pattern, called the polar vortex keeps the cold Antarctic air trapped over Antarctica and prevents it from mixing with warmer air from other regions of the globe as it does other seasons of the year. In addition, the sun does not shine during winter in

Antarctica. This makes winter air doubly cold and the temperature becomes very low, below –80^{0}C which favors the generation of polar stratospheric clouds (PSC) of ice particles[2] (Toon *et* al. 1989). Normally, chlorine and bromine are locked into stable reservoir compounds, such as, $ClONO_2$, $BrONO_2$ and HCl. $ClNO_2$ and HCl play a major part in ozone depletion of the Antarctic stratosphere. The PSC particles interact rapidly with those two inactive chlorine compounds[3,4] (Molina *et* al. 1987; Tolbert *et* al. 1987).

Important reactions are

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$

[5,6,7,8] (Crutzen *et* al.1992; Prather 1992a; Abbat & Molina 1992; Hanson & Ravishankara 1992). The result of these reactions is the transfer of inactive stratospheric chlorine to the potentially reactive forms Cl_2 and HOCl. When sunlight first penetrates the Antarctic stratosphere in the spring, Cl_2 and HOCl are photolyzed, creating a deluge of ozone destroying radicals. Thus, the ozone hole is created over the Antarctic in the spring. However, stratospheric ozone depletion due to bromine is particularly efficient, because bromine stays much longer in its reactive form than chlorine[9] (Rumen 1995). Bromine (Br) plays a dominant role in ozone loss over the Arctic. Volatile brominated products are usually generated by industry and through deforestation activities. HBr can be generated via similar tropospheric cycles as those that generate HCl. HBr is potentially more destructive because of its weaker bond strength. Hanson and Ravishankara demonstrated that HBr was adsorbed at least as efficiently as HCl on an ice surface. Bromine is liberated from a reservoir species HBr, which is converted to a photochemical active form Br_2. Br_2 photolyzes to form Br atoms, which then react with ozone to form BrO, which in turn, is able to destroy additional ozone. Br atoms can not only react with O_3, but also with H_2O to form HBr, effectively short-circuiting the ozone depletion process. It is found that atmospheric bromine is responsible for about 25 % of polar ozone depletion and ozone destruction efficiency by bromine on a per atom basis is about 50 times more than that of chlorine in the lower stratosphere[10] (WMO 1994).

There are two types of polar stratospheric clouds (PSCs). Their identity depends on composition of the cloud particles and the temperature formation threshold. Chemical reactions occurring on the surface of the ice particles in polar stratospheric clouds (PSCs) play a crucial role for the ozone destruction[3,11] (Molina et al. 1987; Solomon et al. 1986). Type I PSCs, observed in the Arctic and Antarctic winters condense at temperatures 2-30 K above the water ice frost point. They are thought to consist of nitric acid and water in the form of nitric acid trihydrate (NAT). The NAT ice particles are significant because they form at temperatures 5-7 K above that at which the pure ice crystal form, appearing earlier in the winter. Type II PSC particles are nearly pure ice in the cold Antarctic winter stratosphere[12] (Tolbert *et* al. 1993).

A single ice nanoparticle has three parts; surface, subsurface and interior[13] (Rowland *et* al. 1995). The surface of ice nanocrystals consists of 3-coordinated molecules with non-H-bonded atoms or dangling –H (D) (d-H (D)), molecules with a dangling-O coordination (d-O) and 4-coordinated surface (s-4) water molecules[14] (Devlin *et* al. 1995). In the interior and the subsurface regions of crystalline ice, each water molecule is coordinated through four H-bonds. Two of them are through the two hydrogen atoms, and the others are through oxygen. However, the three parts of the ice nanocrystals have different vibrational modes[13]. For the surface they are; 1. the out-of-phase stretch of the three coordinated molecules with dangling-H (D) is 3692 (2725) cm^{-1}, the in-phase stretch 3110 (2300) cm^{-1} and the bending mode 1650 (1215) cm^{-1}, 2. the out-of-phase stretch of the three coordinated molecules with dangling-O is 3560 (2640) cm^{-1}, the in-phase stretch 3350 (2480) cm^{-1} and the bending mode 1690 (1235) cm^{-1}. 3. the out-of-phase of s-4 molecule is 3490 (2580) cm^{-1}, the in-phase 3270 (2430) cm^{-1}. These modes cause absorption of infrared radiation of the indicated frequencies and the response of the position of the infrared bands to different adsorbates can be used to characterize molecular interactions with the ice surface. Interior D_2O ice gives absorption in the 2300-2500 cm^{-1} spectral range. In this thesis, the interaction of the adsorbates ND_3 and DBr with the D_2O ice nanocrystals has been investigated by using the difference spectra. The difference spectra were obtained between spectra of bare ice and adsorbate-coated ice. These difference spectra showed the significant shifts of surface-localized ice modes caused by the adsorbed molecules. They also showed that

those adsorbed molecules converted much of the subsurface ice to interior ice[15] (Buch *et* al. 1996).

Previous Fourier-transform infrared spectroscopic (FT-IR) studies have considered three types of molecular adsorbates, such as, a) weak adsorbates (CH_4, N_2, CO and H_2), b) strong H-bonding adsorbates (H_2S, SO_2, HCN andC_2H_2), c) penetrating adsorbates (EO, HCl, and NH_3). However, the information about the surface structure of the ice nanocrystals can be found from the strong H-bonding and weak adsorbates. Penetrating adsorbates, particularly NH_3 in this case, affect the entire ice spectrum as they react with ice nanocrystals to form crystalline hydrates at the cryogenic temperatures. They do not undergo desorption at cryogenic temperatures[16] (Delzeit *et* al. 1997).

FT-IR spectroscopy was also used to monitor the reactions of gas-phase chlorine nitrate, hydrogen chloride and dinitrogen pentoxide with solid ice films at 140-200 K[17] (Horn et al. 1995). FT-IR difference spectra, with a subtract factor of 1.000, is convenient to eliminate most of the strong absorption features of the bulk ice while retaining significant intensity in the bands of the surface molecule modes. FT-IR studies are not the only way by which ice-reactions can be followed. Mass spectrometric (MS) techniques have been essential for determining the nature of any products being evolved from the surface. But MS-based experiments do not provide a direct analysis of the surface species. Spectroscopic analysis of the ice surfaces should be used in conjunction with temperature-programmed (TP) MS to obtain the full picture[17]. This approach presented the interactions of $ClONO_2$, HCl, Cl_2 and HOCl with water-ice surfaces.

The main objectives of the present study are to investigate the interaction between ammonia and the ice surface, namely ND_3 and D_2O; and also DBr and D_2O. Difference spectra have been examined to see the effect of the reactions. Adsorbate SO_2 was also used in the study to examine whether adsorption of ND_3 is reversible or not. CF_4 was only used to determine particle size. Further studies are also required to get more information about ND_3-coated ice surface or DBr-coated ice surface.

Chapter 2

Methodology

This chapter deals with experimental equipment and discusses experimental methods. The equipment that was used in the experiment, will be described below:

2.1 Experimental Equipment

A vacuum system, cryogenic system, a cryogenic cell and the FT-IR instrument have been used in the experiment. Figure1 shows the different sections of the equipment. The function of these items is discussed below:

2.1.1 Vacuum System

A Welch Duo Seal vacuum pump model 1402 and an oil diffusion pump have been used to evacuate the glass manifold. Glass vacuum lines are used to connect the manifold to the outer portion and the inner portion of the infrared sample cell. The connection between the outer portion and the vacuum system provided a vacuum required in order to isolate the inner portion of the cell from vapor thermal transport. The inner portion connection is used to evacuate the cell and allow the gaseous samples to move into the cell. A Hastings thermocouple Vacuum Gauge measures the pressure of this system for which the minimum pressure is ~ 10^{-5} torr. A dual channel Validyne Model CD 223 Gauge with the measurable pressure ranges of 0.01 to 150 and 0.1 to 1000 torr were used to monitor the loading of the gaseous samples.

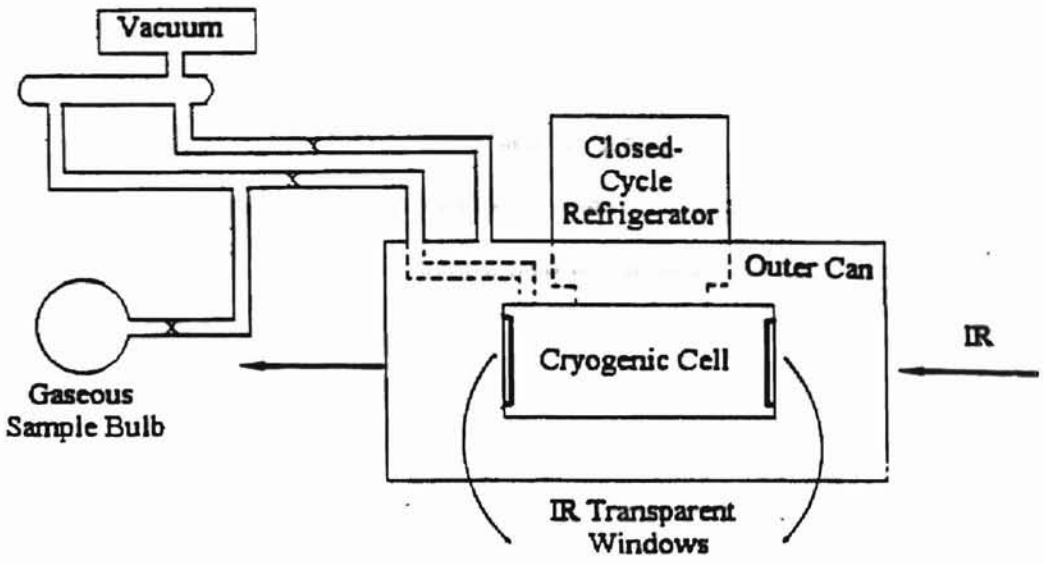

Figure 1. Different components of the experimental equipment

2.1.2 Cryogenic System and Cryogenic Cell

The main component of the cryogenic system is an Air Product Model CS-202 closed cycle helium refrigerator. This system provides a variable amount of refrigeration between room temperature (300 K) and 10 K. The components of the closed cycle cooler are a two-stage expander cryogenic cooler, a compact air-cooled, oil lubricated compressor module with integral oil-cleanup package and an electrical control panel. The compressor is connected to the expander cooler by flexible interconnecting gas lines.

2.1.3 FTIR Instrument

A Digilab FTS-40 model spectrometer was used to collect absorbance spectra that was monitored, stored and manipulated on a Hewlett Packard PC. Since the FT-IR instrument is a single beam spectrometer, a background spectrum was obtained for each series of spectra.

2.2 Experimental Method

The window-deposited-nanocrystals method is used to create the sample composed of a 3-D network of ice nanocrystals. Procedures for this method are as follows: H_2O (D_2O) vapor and carrier gas (N_2) are first loaded into the sample bulb with a molar ratio 1/100 (D_2O/N_2). This gas mixture is loaded into the precooled cell (~135 K) with ~320 torr of the gaseous mixture from the one liter sample bulb expanded into the cell to a pressure of ~250 torr during each loading stage. The loading temperature of 135 K was held constant during the load-evacuation cycles. When the gas mixture enters the cold inner cell, the water vapor in the 1 % gas mixture becomes saturated so liquid droplet form. These droplets crystallize on a short time scale and ~4 % of the nanocrystals become attached to the windows of the cell. A load-evacuation cycle is repeated 50 to 60 times to complete the formation of an assembly of the nanocrystals. The thickness of the resulting network increases with the number of loading cycles, as observed with FT-IR spectroscopy as increasing peak intensities. One of the important characteristics of the ice nanocrystals is reproducibility of the spectra.

Before adding the mixture to the cell, a background spectrum was taken. After the deposition was completed, the sample was cooled to 120 K. Then the bare ice spectrum was obtained. The intensity of d-D ice surface and interior D_2O bands was noted to characterize the

sample. Because ND_3 was less volatile than DBr, the temperature of 120 K was used for its adsorption and reaction to allow uniform exposure of the nanocrystals to the vapors of the adsorbate. A metal needle valve was used in the loading section, to control the flow of ND_3 or DBr to the ice surface. The amount of ND_3 or DBr added to the cell was monitored by measuring the dynamic flow pressure which was held near 4×10^{-4} torr. The flow of ND_3 or DBr was continued until d-D sites (2725 cm^{-1}) were completely covered, which is called the 1st saturation level. Exposure of ND_3/DBr continued with attachment at d-o and s-4 sites and d-D band shifted to lower frequency range. This was the 2nd saturation level. As reaction commenced, the particles started losing interior ice, which was the 3rd saturation level. Different adsorbates, such as Carbon Tetraflouride (CF_4), Acetylene (C_2H_2), and Sulfur Dioxide (SO_2) have also been added to the cell at 85 K, 110 K and 120 K respectively. The longitudinal band of the CF_4 spectra is indicative of the particle size and SO_2 shows whether adsorption of ND_3 is reversible or not. For DBr, the ice sample was made at 135 K and then the temperature was set at 120 K for exposure to DBr. During these processes, spectra of bare ice and adsorbate-coated ice were taken. Then the bare ice spectrum was subtracted from spectra of ice with the adsorbate that was collected as a function of time. All these spectra reflect the conversion of the surface to a shifted-surface spectrum and the subsurface molecules into interior ice molecules. Spectra have been measured at a nominal 4 cm^{-1} resolution, by using 100-400 scans with a Bio-Rad FTS-40 spectrometer.

There is another way ND_3 and DBr can be loaded in the cell by using two separate loading ports in the system. In one port, ND_3 and N_2 and in the second port, carrier gas (N_2) and D_2O can be loaded to the cell. Each type of particle can be added alternately to the cell. The ratio of this alternate loading could be 1:1. This alternation may result in the intimate mixing of the ice and adsorbate particles. But, the latter procedure has not used in obtaining the data of the thesis.

Chapter 3

Results and Discussions

Absorption of ammonia and deuterium bromide to the ice surface, resulted in shifted surface, subsurface relaxation and generation of interior ice. Loss of interior ice and gain of some lower hydrates were also observed during the study. Ammonia molecules exhibited molecular interaction, whereas deuterium bromide molecules showed both covalent and ionic interaction. Some strong and intermediate H-bonding adsorbates, such as SO_2, and C_2H_2 were introduced at different levels of exposure. Adsorbate CF_4 was also exposed to the ice surface. Before the exposure of any adsorbates to ice surface, one had to take a reference spectrum.

The behavior of the adsorbed ammonia on the ice surface is strongly dependent on the level of exposure, the isotopic composition, and the temperature. In the present study, the ice nanocrystals were gradually saturated or covered with ammonia at 120 K. Their infrared spectra at different levels are presented in Figure 2.

In curve (a), exposure of D_2O ice to ND_3 at 120 K resulted in strong hydrogen bonding of the ammonia to the dangling-deuterium (d-D) site at 2725 cm^{-1} as shown by the loss of intensity in that band. Here positive bands reflect the gain of a component, while negative bands indicate loss of a component due to the addition of adsorbate. More limited uptake occurred at the dangling-oxygen (d-O) and 4-coordinated (s-4) surface sites. As ammonia is a proton acceptor, it preferred to form strong hydrogen bonds at d-D sites. The peak intensity of d-D was .0011 before the exposure to ND_3, but the increasing exposure of ammonia gradually diminished d-D site intensity, producing the loss band in curve (a) at 2725 cm^{-1}. With further exposure, ammonia (ND_3) molecules continued associating with the other surface sites (s-4, d-O), bonding weakly with them. Then band intensity for these sites began to shift to a lower frequency range mainly from occupation of s-4 sites by ammonia. This was the 1st saturation level. Then, ND_3 fully coated the ice surface passing the 1st saturation level, exhibiting subsurface relaxation and

generating new interior ice in curve (b). This was recognized as an indirect effect of strong adsorbate interaction with the irregular ice surface. As the exposure of ammonia continued, the d-D band originally at 2725 cm^{-1}, was shifted to low frequency range below 2300 cm^{-1}. The subsurface continued to relax and the interior ice kept growing at the 2^{nd} saturation level (mentioned in chapter 2) as the amount of adsorbed ammonia increased. After exposing for 2 hrs. the mixture was left for overnight; it was found that more subsurface was relaxed and new interior ice was generated, which indicated in curve (c). Then exposure of ND_3 to the ice surface was continued, that was reflected in the spectrum (d), which showed the first sign of penetration of ND_3 into the ice surface and the loss of interior ice, which was the 3^{rd} saturation level as stated in chapter 2. There was a ND_3 band at 2530 cm^{-1}, which kept growing as exposure continues. Neither proton transfer nor Ostwald ripening, which is used to transform the nanocrystals to a larger average size without a change in the total amount of the ice, occurred during the process (Delzeit *et* al. 1997). When the ammonia concentration was high, D_2O nanocrystals were converted to crystalline $ND_3.D_2O$ hydrate. There was an intense broad band that appeared below ~2250 cm^{-1} due to ND_3 bonding with water in the hydrate.

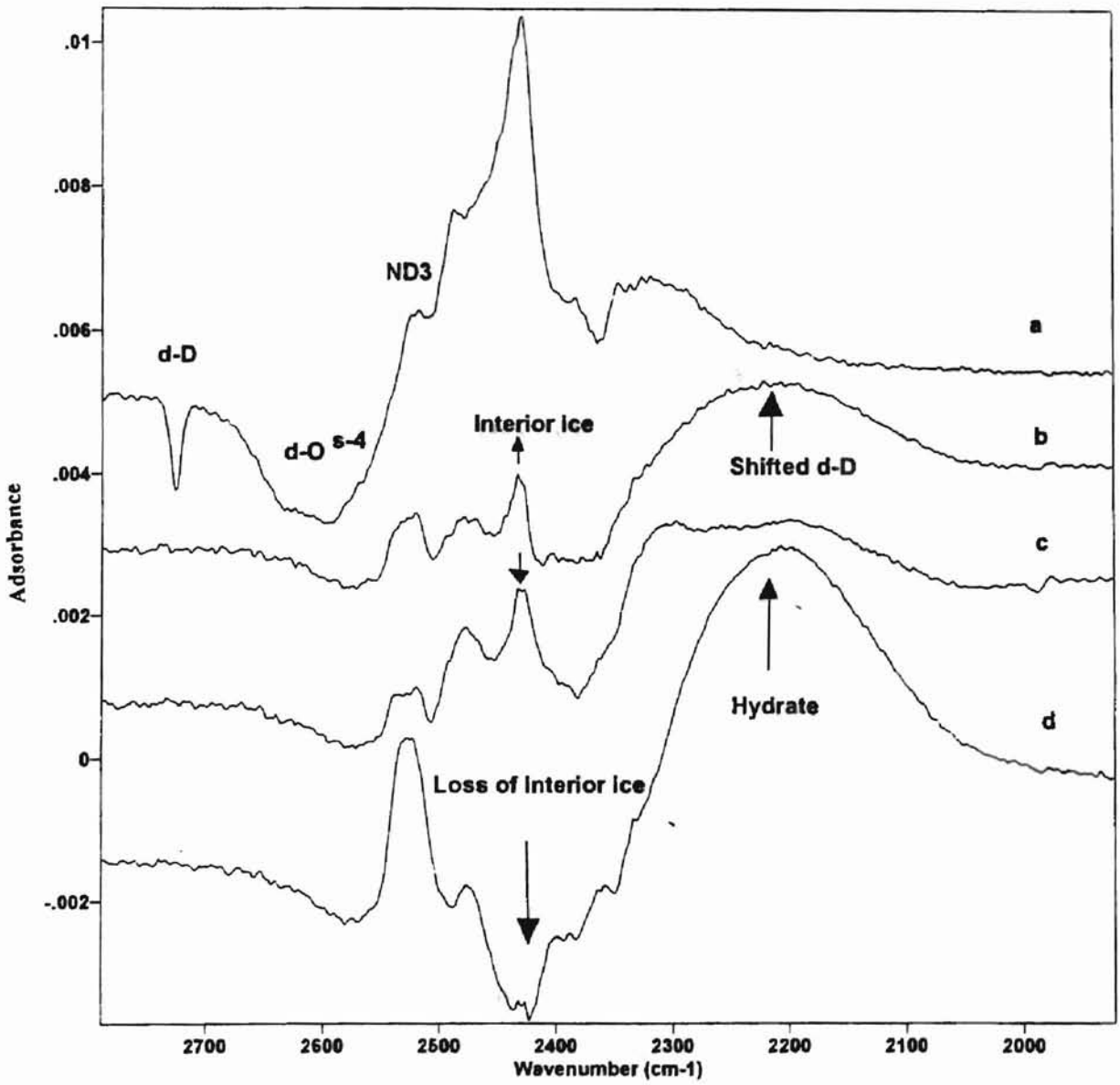

Figure 2. 4 stages of ND_3 on D_2O at 120 K; d-D saturation; 2nd saturation level; subsurface relaxation and reaction.

Figure 3 represented various infrared spectra of ND_3 and acetylene (C_2H_2) –coated ice surface at different temperatures. Curve (a) showed that d-D band was completely saturated with ND_3 at 120 K after 1 hr. 40 min. of exposure. This was the 1st saturation level. The temperature was then reduced to 110 K and the ND_3 coated ice surface was exposed to acetylene (C_2H_2) vapor. About 3 hrs. later, the acetylene C≡C stretch band appeared at 1958 cm^{-1} and a strong broad band appeared around 2220 cm^{-1} due to shifting of intensities of the d-D sites, which showed in curve (b). Since C_2H_2 is a relatively strong proton donor, the acetylene attached at vacant d-O and s-4 sites of the surface. Adsorbed acetylene molecules appeared to stabilize a linear stronger D-bonded structure of the ammonia molecules at the d-D sites. The D-bond of ammonia is strong in presence of neighboring adsorbate molecules, but in the absence of those molecules, they become weak and bend on the surface. That shifted the d-D vibration to lower frequency. As a result of C_2H_2 inducing further order some interior ice band growth also occurred. The mixture was pumped overnight. The reversal of curve (b) was observed in curve (c). The C_2H_2 band was mostly gone. After removing the C_2H_2, SO_2 was added to the cell. After a few hours, there was a strong uptake of SO_2 at the d-D site as shown by the band at 2673 cm^{-1} in curve (d). ND_3 might be replaced by SO_2 on the ice surface and d-D band shifted to the known d-D - - SO_2 position.

The antisymmetric-stretch band of adsorbed Carbon tetraflouride (CF_4) is shown in Figure 4 (Devlin *et* al. 1997). In this case, the sample temperature was reduced to 85 K. The curve of Figure 4 revealed the dominant transverse band at 1242 cm^{-1} and longitudinal band at 1322 cm^{-1} as CF_4 was added to the ice nanocrystals to saturation level. The strength of the 1322 cm^{-1} band is a good indicator of amount of adsorbed CF_4; which, in turn, indicates particle size. Since 20 nm particles are known to give ~0.12, for similar ice sample the peak value of .05 showed ice particles are ~50 nm in size.

Figure 5 showed the infrared spectra of DBr on ice nanocrystals at 120 K. After adding DBr for 1hr. 6 min., the 1st saturation level was reached, which showed in curve (a). In curve (b), due to ionic mechanism, some lower hydrates formed after d-D band shifted to lower frequency range. In both curve (a) and (b), the strong loss near 2370 cm^{-1} showed that subsurface

relaxation continued, which generated new interior ice. There was no net interior ice lost during that period. But curve (c) showed the loss of interior ice. As, DBr molecules are highly reactive and volatile, they penetrated the ice surface, which caused the loss of interior ice. In this study, relaxation dominated in curve (a) and in curve (c) reaction became a dominating factor.

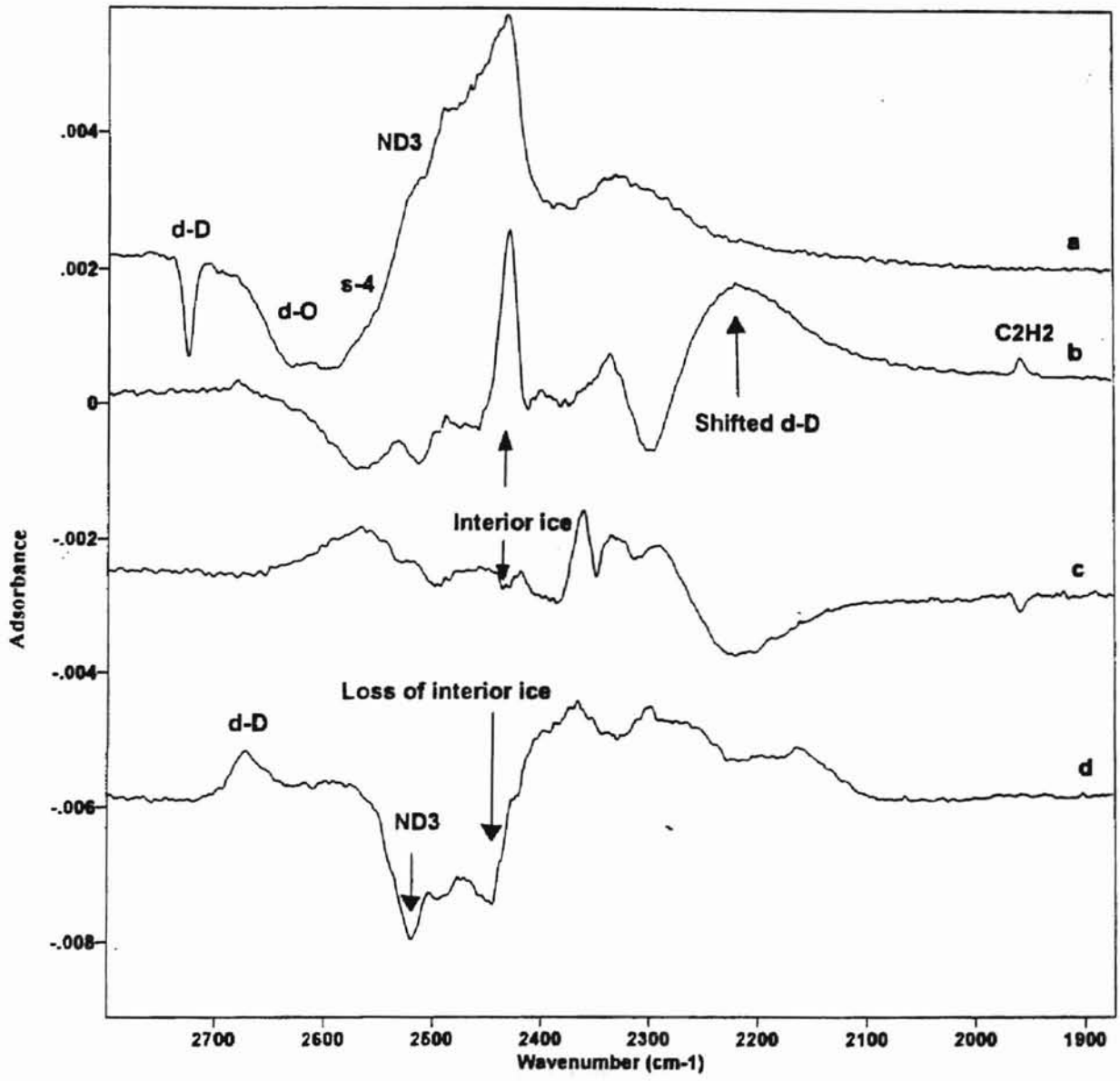

Figure 3. Spectra of d-D saturation with ND_3; C_2H_2 saturation; removal of C_2H_2; added more ND_3 and SO_2.

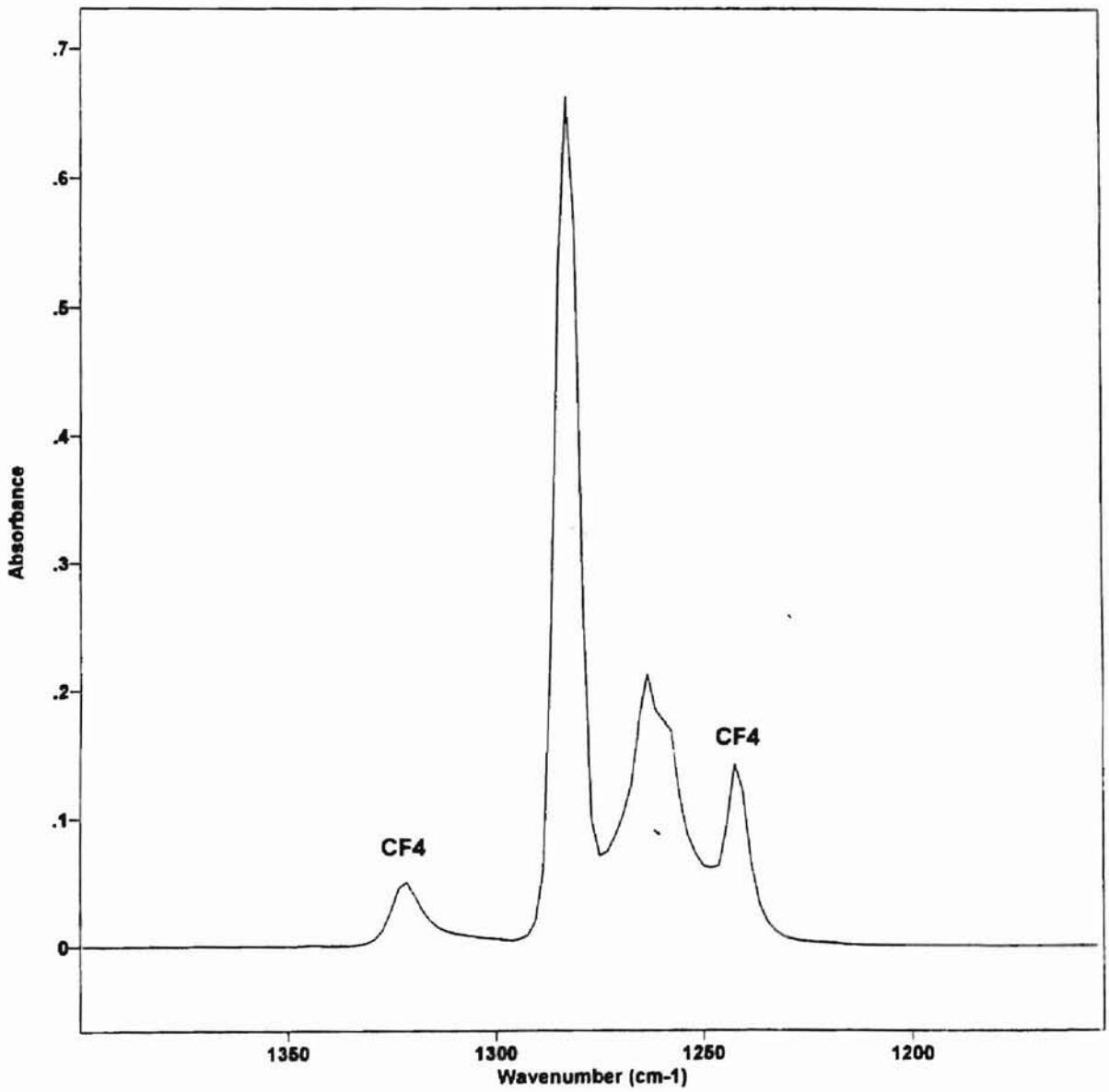

Figure 4. CF_4 effects on ND_3-coated ice surface at 85 K

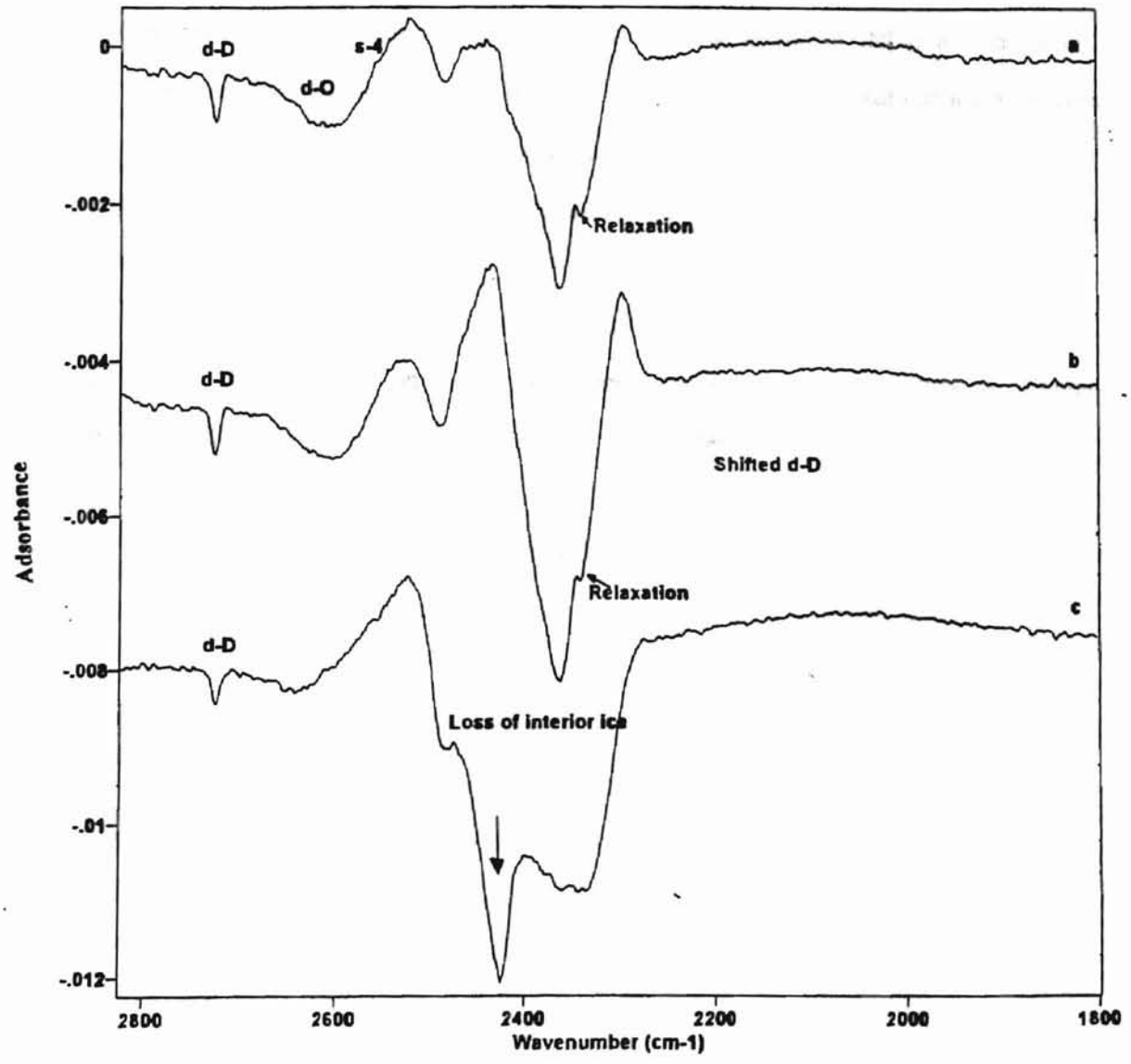

Figure 5. Spectra of ice/nanocrystals exposed to DBr at 120 K.

Summary

This study has demonstrated the conversion of the ammonia (ND_3) and deuterium bromide (DBr) monolayer-coated ice surface to shifted surface and the ice subsurface molecules into interior ice molecules. Conversions of ice to hydrates have also been observed in this study. It was observed that these conversions proceeded through a molecular (ND_3) and an ionic (DBr) mechanism.

A heterogeneous gas-solid process is responsible for these conversions. But the behavior of the adsorbed ammonia and deuterium bromide on the ice surface is strongly dependent on the level of exposure and the temperature. Spectra with ammonia and hydrogen bromide have been measured as a function of exposure and time near 120 K. Some intermediate H-bonding and weak adsorbates have been used in the present study, such as, SO_2, C_2H_2, and CF_4. Adsorbate SO_2 was used to study whether adsorption of ND_3 is reversible or not. It is found that ND_3 was replaced by SO_2 on the ice surface. CF_4 was used to measure particle size. It was observed that the strength of CF_4 bands indicated particle size of ~50 nm. Adsorbate C_2H_2 is a strong proton donor to oxygen of the surface with C≡C stretch band observed at 1958 cm^{-1}

A penetrating adsorbate, DBr was introduced in this study. As the nature of the ice surface at 120 K was dynamic, DBr molecules near the surface might be ionized. DBr, like other strong and intermediate adsorbates causes subsurface ordering to form interior ice. When DBr exposure continued, interior ice began to be lost as the DBr hydrate formed. Also exposure of ammonia must pass the 2^{nd} saturation level before it forms hydrate ($ND_3.D_2O$).

In both cases, there was a phase transition between ice and hydrate phase. The first step for the formation of the hydrate is the nucleation of the hydrate phase. It took more than one layer of exposure of adsorbates (ND_3/ DBr) to promote nucleation. Experimental results for ND_3 showed the conversion of the ice nanocrystals to hydrate via a molecular mechanism. The adsorbed ND_3 must have sufficient energy to cross the critical nucleation point before it forms hydrate.

It was mentioned before, when the ice surface was coated with ammonia or deuterium bromide, reactions did not occur initially. As exposure continued, the reaction was initiated. As a

result, these adsorbates start penetrating the ice surface and the interior ice began to decrease and at a certain point hydrates began to form.

It was originally suggested that PSCs particle might lead to an alteration of the chlorine chemistry in the Antarctic stratosphere. They also occurred only sporadically in the warmer Arctic. PSCs are not like the clouds that usually observe in the sky, because they contained ice crystals. The clouds that did form were mostly type I nitric acid trihydrate and water ice type II particles. Composition of the cloud particles can be changed due to chemical reactions. When ice crystals formed, two compounds such as, nitrogen oxide (NO_x) and chlorine, which are found normally in the air, get incorporated into the ice crystals. Usually people use chlorine in the swimming pools. But these two compounds are radical forms. Instead of being floating around in the air, they dissolved in the ice. The PSC particles react rapidly with these two compounds and they become reactive. In the spring, when sunlight penetrates, they are photolyzed and start destroying ozone. In our case, the particles in the atmosphere are in the different forms, such as, acids, bases, water vapor or hydrates. When acid is coated with ice surface for a certain amount of time, then the whole surface begins to saturate. Due to nucleation process, hydrates begin to form. This is a phase transition between ice and hydrate phase. It is required further studies in this regard.

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